FINAL REPORT

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Medical Department
3M Company
St. Paul, MN 55144

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Title: Biomonitoring Assessment of the 3M Cottage Grove Building 15 Demolition and Disposal Project. Phase II

Study
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Summary

A total of 25 subjects who worked on the 3M Cottage Grove Building 15 demolition and disposal project had baseline and end-of-project perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) measurements. These subjects did not include those workers who were involved with the removal of equipment and line that was done earlier. Those results will be presented separately. The 25 subjects' baseline mean PFOA concentration was 3.5 ng/mL (95% CI 3.0 – 4.0) and their end-of-project mean PFOA concentration was 4.8 ng/mL (95 CI 3.9 – 5.7). The baseline mean PFOS concentration was 16.1 ng/mL (95% CI 12.8 – 19.4) and the end-of-project mean PFOS concentration was 15.1 ng/mL (95% CI 12.3 – 17.9). The mean paired concentration difference (baseline minus end-of-project) for PFOA was +1.3 ng/mL ($p = 0.004$). Likewise, the mean paired difference for PFOS was -1.0 ng/mL ($p = 0.10$). Thus, there was minimal (1 ng/mL) increase in PFOA and no evidence of an increase in PFOS concentrations from baseline to end-of-project measurements. Conclusion: Based on the paired biomonitoring data, there was no substantive occupational exposure to PFOA or PFOS while working on the 3M Cottage Grove Building 15 demolition and disposal project.

Introduction

Several remediation projects were launched in 2009 regarding legacy perfluorochemicals. These included the 3M Woodbury landfill remediation project, the 3M Cottage Grove Buildings 15 and 73 demolition and disposal project (hereafter referred to as only Building 15), the 3M Cottage Grove Building 25 re-roof project, the 3M Cottage Grove D1/D2 excavation project, and the 3M Decatur Building 2/49 demolition and disposal project. For each of these projects baseline and end-of-project assessments were required of 3M employees and contractor workers who entered specified work zones where potential exposure to legacy perfluorochemicals (e.g., PFOA (perfluorooctanoate) and PFOS (perfluorooctanesulfonate)) was possible, but due to the uniqueness of the work the magnitude was unknown. Both baseline and end-of-project assessments required a worker's response to a medical questionnaire and collection of blood for serum measurements of PFOA and PFOS, and analysis of several clinical chemistries. The purpose of this report is to provide a descriptive analysis of the PFOA and PFOS serum concentrations (ng/mL) at baseline and end-of-project time periods for the 3M Cottage Grove Building 15 demolition and disposal project. Results for those workers who were involved with equipment and line removal from Building 15, that was conducted prior to the demolition of Building 15, will be presented in a separate report.

Methods

1. Informed consent

The purpose of the project was explained in an informed consent. Subjects read and signed this informed consent at both baseline and end-of-project assessments. Subjects were informed they could not work on this specific project without such compliance.

2. Clinical chemistries

Clinical chemistries included a lipid panel profile, blood glucose, BUN, creatinine, serum electrolytes, and liver enzyme tests (including alkaline phosphatase, AST, ALT, and total bilirubin). Fasting was not a requirement because of the logistics of collecting blood samples during various times of the day. Clinical chemistries were analyzed by Quest Diagnostics. Individual clinical chemistry analyses at baseline and at end-of-project were medically reviewed by Dr. Gibson. Subjects were informed in writing that this examination program was not a full medical 'check-up.' Values out of reference range were indicated with a notation for the subjects to follow up with their primary care physician if they had abnormal test results. However, questions could be directed to Dr. Gibson regarding their clinical chemistry test results should the subject so desire.

3. Analytical measurements of PFOA and PFOS

Serum samples were analyzed for PFOA and PFOS by state-of-the-art high performance liquid chromatography mass spectrometry methods by the 3M Medical Department's Toxicology Laboratory under the direction of Dave Ehresman. Medical Department personnel collected

blood samples that were processed to provide serum samples for analysis. These samples were assigned unique identification numbers and randomized prior to the samples being delivered for analysis. The 3M Medical Department's Toxicology Laboratory was "blinded" to the identity of all samples received for analysis.

Sample extractions were performed using solid phase extraction (SPE) technique. The extraction and sample clean-up was based on a 100 uL sample size and utilized Waters (Milford, MA) Oasis® hydrophilic–lipophilic balance (HLB) 3.0mL cartridges (Ehresman et al. 2007).

The method used two stable labeled internal standards for quantitation. The internal standards used were a dual labeled PFOS where two ^{18}O molecules were included in the sulfonate group (internal standard, >99% purity, synthesized by Research Triangle Institute, Research Triangle Park, NC) and a dual labeled PFOA molecule, where the carboxyl and alpha carbons were labeled with ^{13}C stable isotope (greater than 97%, provided by DuPont, Wilmington, DE). All quantitations were based on matrix matched extracted standard curves.

A 5 uL injection of the sample eluate was introduced into the High Pressure Liquid Chromatograph (HPLC) which was directly interfaced into the triple quadrupole mass spectrometer (Applied Biosystems/MDS-Sciex Instrument Corporation, Forest City, CA). Standard curves covered the range from 1.0 - 150 ng/mL. Standard curves were evaluated using a quadratic regression model where the standards were weighted at 1/x, and each curve had an ''R'' value equal to or greater than 0.9998. Matrix spiked controls (QC samples) evaluated during this study all had acceptable results "with-in" their previously established ranges. Matrix-matched dilutions were used for samples requiring dilution to bring the samples into the linear range of the assay. Extracted serum and aqueous blanks remained below the lower limit of

quantitation established at 1.0 ng/mL (lowest standard fitted on the standard curve used for this project).

4. Communication

After each blood collection, individual letters were sent to the participants describing their results. In the baseline assessments, two letters were sent. One referred to the clinical chemistries and the other letter provided baseline PFOA and PFOS concentrations. At end-of-project, two letters were again sent to each participant. The first letter provided the individual's clinical chemistry results. The second letter compared baseline to end-of-project serum PFOA and PFOS concentrations.

Results

Table 1 provides the total number of individuals, by company, who were tested for PFOA and PFOS during the 3M Woodbury landfill remediation project.

Table 1. Distribution of workers by company and participation

Company	Baseline	End-of-Project	Reason for No End-of-Project Sample
Veit	25	24	Did not appear at blood collection (n = 1)
MetroGravel	2	1	Did not work at site (n = 1)
Other	4	0	Did not appear at blood collection (n = 1)
			Did not work at site (n = 3)
Total	31	25	

Tables 2 and 3 provide the measures of central tendency for the baseline and end-of-project PFOA and PFOS concentrations for those 25 subjects with paired measurements (baseline and end-of-project). Values are provided in ng/mL (parts-per-billion).

Table 2. PFOA Baseline and End-of-Project Concentrations (ng/mL)

						Arithmetic		Geometric	
	Min	Q1	Median	Q3	Max	Mean	95% CI	Mean	95% CI
Baseline	1.3	2.5	3.7	4.5	5.5	3.5	3.0 – 4.0	3.2	2.7 – 3.8
End-of-Project	1.5	3.4	4.6	5.9	9.8	4.8	3.9 – 5.6	4.3	3.6 – 5.0

Table 3. PFOS Baseline and End-of-Project Concentrations (ng/mL)

						Arithmetic		Geometric	
	Min	Q1	Median	Q3	Max	Mean	95% CI	Mean	95% CI
Baseline	5.8	10.1	13.6	21.7	33.7	16.1	12.8 – 19.4	14.5	11.9 – 17.6
End-of-Project	6.5	10.1	12.6	18.8	32.1	15.1	12.3 – 17.9	13.8	11.6 – 16.4

Because the data were paired samples, a matched-paired statistical analysis was performed where the mean difference is the average of the sum of the individual differences for the 25 subjects . See Equation 1.

Equation 1.

$$\text{Mean Difference} = \sum_{i=1}^{25}(\text{end-of-project} - \text{baseline})/25$$

Because of the skewed PFOS distribution, in particular, as seen in Table 3, the mean differences of the natural logs of the paired values were also determined. See Equation 2.

Equation 2.

$$\text{Mean} = [\sum_{i=1}^{25}[(\ln(\text{end-of-project value})) - (\ln(\text{baseline value}))/25]$$

Results for *Equation 1 and Equation 2*, and associated statistics of the mean differences of the paired comparisons, are provided in **Table 4** for both PFOA and PFOS.

Table 4. Matched-pair Analysis Comparing Baseline to End-of-Project PFOA and PFOS concentration (ng/mL)

Mean Paired Difference	PFOA (ng/mL)	t-ratio	p value	PFOS (ng/mL)	t-ratio	p value
Equation 1	+1.3	3.16	0.004	-1.0	-1.72	0.10
Equation 2	+0.3	3.30	0.003	-0.04	-1.38	0.18

Only for PFOA was there an increase in the mean of the paired differences although this 1.3 ng/mL difference was not substantial, given the analytical variability of the methods used. No increase was observed for PFOS. Similar results were seen when the differences between the logs were analyzed.

Figures 1 and 2 provide another method to compare the baseline to end-of-project concentrations for PFOA and PFOS, respectively. [Note: These figures are graphed on a log scale.] A strong linear relation centered along the diagonal is indicative of no change between the paired measurements. The R^2 was 0.03 for PFOA (Figure 1) and 0.87 for PFOS (Figure 2). The lack of a strong linear relation with PFOA is the result of an increase in 11 workers' end of project concentrations over their baseline as shown in Figure 1. These 11 workers are found in Figure 1 above the depicted identity line where y = x (i.e., end of project = baseline).

Discussion

Comparison of baseline and end of project serum concentrations of PFOA and PFOS provided each worker an excellent method to assess his/her exposure experience for the 3M Building 15 Demolition and Disposal Project. Given the fact that exposure potential during the course of the demolition project was unknown, the use of biomonitoring data allowed for an assessment of the actual (unknown) exposure to PFOA or PFOS, or to materials that may degrade to them. The clinical chemistry data were not analyzed by paired statistics because the biomonitoring data indicated there were no substantive differences in exposure to PFOA or PFOS between the baseline and end-of-project measurements. Potential exposure to any other materials would not be known since only PFOA and PFOS were analyzed in the workers' serum. The lack of any change in PFOS concentrations between baseline and end of project is likely due to the fact that, unlike PFOA and its salts, PFOS had not been manufactured in Building 15 for several decades.

Conclusion

Based on paired biomonitoring data, there was a slight average increase (approximately 1 ng/mL) in PFOA serum concentrations for the 25 workers who had paired baseline and end of project measurements involved with the 3M Buidling15 Demolition and Disposal project. This was not considered a substantive change in serum PFOA concentrations. There was no difference in PFOS concentrations.

References

Ehresman DJ, Froehlich JW, Olsen GW, Chang SC, Butenhoff JL. 2007. Comparison of human whole blood, plasma, and serum matrices for the determination of perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and other fluorochemicals. Environ Res 103:176-184.

Figure 1. 3M Cottage Grove D1/D2 Remediation Project:
Baseline vs. End of Project PFOA Concentrations (ng/mL)

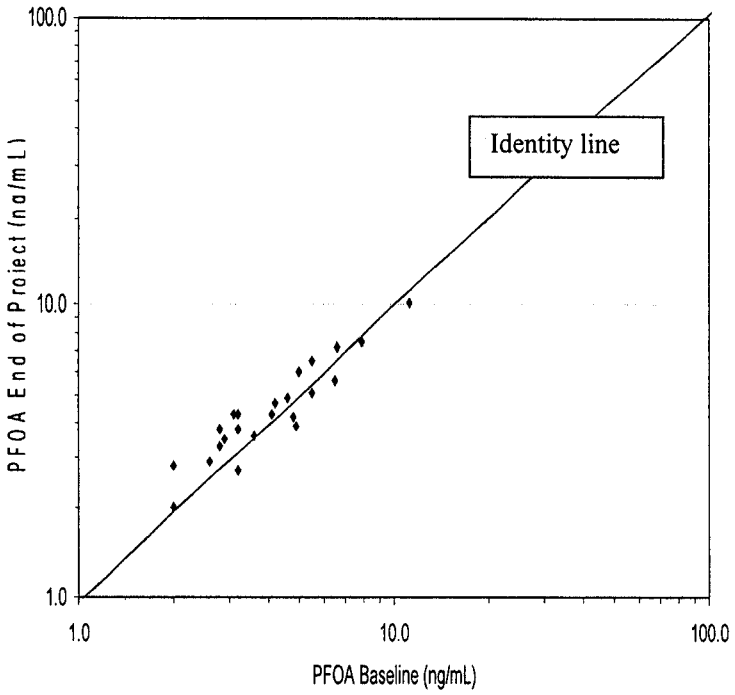

Figure 2. 3M Cottage Grove D1/D2 Remediation Project:
Baseline vs. End of Project PFOS Concentrations (ng/mL)